PHOTOCHEMICAL WEATHERING AND CONTEMPORARY VOLATILE LOSS ON MARS.
R.L. Huguenin, Geology/Geography, University of Massachusetts, Amherst, MA 01003.

In an earlier series of papers by the author it was proposed that photochemical weathering of Fe^{2+} in magnetite (1,2) and in mafic silicates (3) may be occurring in the contemporary surface environment with a resultant loss of O_2 from the atmosphere (4):

$$2FeO_{surface} + \tfrac{1}{2}O_{2atmosphere} + h\nu \rightarrow Fe_2O_{3surface} \quad (1)$$

It was estimated that a net loss of 10^{25}-10^{28} molecules cm^{-1} could have occurred over geologic time. If the O_2 were lost at the expense of H_2O, this would correspond to a loss of 10^0- 10^3m of ice over geologic time (4). Several lines of evidence from Viking lander and orbiter measurements as well as Earth-based telescopic observations support the occurrence of such a contemporary process on Mars. (5).

Morris and Lauer(6) challenged the photochemical weathering model, proposing that oxidation by radient heating rather than UV photoelectron-emission-induced oxidation may have dominated in our experiments. They based this on an experiment whereby unfiltered radiation was able to produce nearly complete oxidation of their samples, while IR-filtered xenon radiation produced no observable oxidation. Their unfiltered radiation produced very high temperatures, while the filtered radiation did not. The authors stated that the filtered and unfiltered irradiances were similar to within a factor of two at 350nm, and they deduced that the high temperatures of the unfiltered radiation drove the reaction.

Subsequent laboratory studies of photochemical weathering of magnetite described here support the original proposal that UV illumination can indeed drive the oxidation of magnetite under contemporary Martian surface conditions. The negative results of the Morris and Lauer (6) study can now be explained.

Samples of reagent grade precipitated magnetite (0.5g) from Fisher Scientific and Pfizer were used for the new experiments. The former sample was cation deficient and the latter was close to stoichiometric, as discussed by Morris and Lauer (6). Samples were placed in an environmental chamber consisting of a hollowed out (1¼" diameter x 3/8" depth) 2 3/4" Varian Conflat blank flange coupled to a 2 3/4" Varian Conflat Sapphire View Port flange using a copper compression gasket. Thermocouples, cooling and heating cartridges, and gas lines were fitted into the chamber, which was interfaced to a Varian ultrahigh vacuum system. The chamber provided horizontal sample orientation to minimize physical disturbance of the exposed sample surface throughout the experiment. The sample chamber was fitted to a sample port at the base of a prototype 3" integrating sphere within a Perkin Elmer 330 dual beam spectrophotometer (185-2600 nm). References and the integrating sphere coating were both Halon.

Samples were illuminated using a PRA Model 6100C microsecond pulsed UV source, which has a thyratron-gated 1.5μs pulse width (FWHM) and programmable pulse frequency. The output spans from 200-2000 nm with peak power at 300 nm (40% of total power output is at 200-500 nm). Samples were illuminated through selected Oriel Optics band pass and long pass filters. Samples were illuminated at pulse frequencies of 2.7 or 4.5 pulses per second (p/s), depending on the experiment, and reflectance spectra of the samples were measured periodically every 1-3 days. Peak pulse power varied depending on the filters used. The unfiltered source had 3kW peak power per pulse, which corresponded to 12.1 mW/cm^2 at 2.7 p/s and 202.2 nW/cm^2 at 4.5 p/s. A long pass filter with a 50%

transmission cut-on wavelength at 530 nm (Oriel Model 5130) yielded 1.3kW peak power per pulse. A UV band pass filter with a center at 325 nm and band width (FWHM) of 200 nm (IR-blocked) (Oriel Model 5165) yielded a peak power of 0.68kW per pulse. At 4.5 p/s pulse frequency, the UV filter produced 4.6 mW/cm^2 average power.

By using narrow pulse widths (1.5μs) and low pulse frequencies, the thermal component of incident radiation was low (flux at 1100 nm is ∿10% the flux at 350 nm) and samples could cool to near-ambient surface temperatures between pulses.

In situ reflectance spectra of the illuminated sample surface provided a sensitive means of detecting and monitoring oxidation. Spectra were periodically measured, and the spectra were divided by the starting (pre-illumination) spectrum to reveal changes. As discussed originally (1,2), a sensitive measure of oxidation of magnetite is provided by a reddening of the spectrum over the 350-750 nm wavelength range. By keeping the sample undisturbed physically, only the UV-illuminated surface layer is measured and surface scattering properties are held constant. A layer of Fe_2O_3 less than 1 micrometer thick can be detected.

Exposure of the Fisher Scientific (Lot 724199) magnetite sample to unfiltered radiation in ambient laboratory air at 20°C revealed a systematic reddening of the sample that became visible in the ratio spectra (scaled to 1.0 at 350 nm) between the fifth and eighth days of exposure. In a second experiment, using a fresh 0.5 g sample from the same lot, but this time inserting the UV filter, reddening again occurred to the same extent after a similar exposure period, i.e., after 6-9 days. A third fresh sample from the same lot was illuminated using the long pass filter, and this time there was no detectable reddening after 49 days of illumination, at which point the experiment was terminated. The three experiments were repeated and the results were confirmed.

A second set of experiments were performed using samples of the Pfizer (Lot E1531) magnetite. As for the Fisher Scientific samples, the unfiltered radiation and radiation using the UV filter both produced detectable significant reddening after similar illumination periods. The length of time required to produce the equivalent reddening, however, was approximately six times longer than for the Fisher Scientific sample, viz. 32-54 days, using the same pulse frequency (4.5 p/s).

In these experiments, illumination through the UV filter was 85-95% of the intensity of the unfiltered radiation over the 200-330 nm wavelength range. Between 330 nm and 400 nm attenuation was appreciable, reaching 10^{-5} at 400 nm. Overall power was reduced, using the UV filter, to 23% of the power of the unfiltered radiation. Illumination through the long-pass filter, by contrast, attenuated total power by only a factor of 2.3 (42% of the power of the unfiltered radiation), with greater than 92% transmission at wavelengths longer than 550 nm. At wavelengths shorter than 520 nm, however, attenuation was total ($<10^{-5}$% transmission) with the long-pass filter. The fact that the illumination through the UV filter produced apparent oxidation at approximately the same rate as unfiltered radiation, while illumination through the long-pass filter produced no observable change after 3-5 times longer illumination, suggests that the reaction was probably controlled by radiation in the 200-330 nm range. This supports the original findings that the reaction is driven by UV illumination at wavelengths shorter than ∿350 nm.

An independent investigation was recently carried out by M. Schaefer (unpublished) at MIT. A magnetite sample was illuminated using a low-power 2.5 watt source, of which the sample intercepted 4 mW. If all the power were

absorbed with 100% efficiency, the maximum sample temperature that would have been possible was 29°C, well below the thermal oxidation threshold. Oxidation was observed to occur after 30 h of illumination (photon flux of 5×10^{15} photons/s intercepting the sample as λ = 253.7 nm line). About 1% of the sample was observed to oxidize to Fe_2O_3, using Mossbauer spectroscopy as the detection technique. In addition to providing independent evidence that the oxidation proceeded non-thermally, the quantum yield was determined to be $\sim$0.1, which was in good agreement with the quantum yield proposed by Huguenin et al (9) for radiation at that wavelength.

Another critical test was performed by a separate laboratory at MIT (8), and independently confirmed by a team at IBM Research Labs (9). The original study (1,2) deduced from the kinetics that photoelectron emission from the Fe^{2+} was occurring as a critical step in the process. It was argued that it occurred with a work function of 3.8-4.2 eV and a quantum yield of $\sim$0.1 electron/photon at 195 nm. This was the first time that photoemission of electrons was proposed to occur from Fe^{2+} in magnetite, and it was deduced to be the most critical and unique step in the process. Poole (8) designed an experiment to detect photoelectron emission from Fe^{2+} in minerals, and he experimentally confirmed that photoelectron emission did indeed occur with magnetite with a work function of 3.9 $\pm$0.1 eV. The quantum yield was also in agreement with predictions. Bagus et al (9) similarly determined a photothreshold of 3.9$\pm$0.3 eV in a combined photoelectron-spin-polarization (ESP) and UV and far-UV photoemission spectroscopy (UPS and FUPS) study of magnetite.

These independent studies support the findings reported here, and suggest that photochemical weathering of magnetite can be UV-induced as originally proposed (1,2,3). The findings are in disagreement with the conclusions of Morris and Lauer (6), and two factors can be cited that may account for the disagreement.

The most important factor seems to be that Morris and Lauer may have not irradiated the samples long enough with the unfiltered radiation to produce detectable oxidation. In particular, examination of the spectral curves for the filtered and unfiltered radiation revealed that the flux differences were greater than claimed by Morris and Lauer. The spectral radiances were published by Morris and Lauer. The wavelengths significant for photooxidation are 195 nm - 350 nm (1,2). Inspection of their figure shows that only at 350 nm are the fluxes of the filtered and unfiltered radiation within the factor of 2 claimed by Morris and Lauer. By 230 nm the fluxes are different by a factor of 60. Extrapolations to 200 nm indicate that filtered fluxes were $> \sim$100 times lower than the unfiltered fluxes. The shorter wavelengths produce the more significant quantum yields for photooxidation ($\sim 10^{-7}$ at the 350 nm threshold to $\sim 10^{-1}$ at 200 nm) (7). Scaling the irradiation periods needed to produce oxidation with unfiltered radiation to these lower fluxes would require irradiation periods that were longer than those used by Morris and Lauer with the filtered radiation.

A second factor is the low sensitivity of their oxidation detection technique. To detect oxidation there would need to be a minimum of between 3% and 15% conversion to Fe_2O_3 (1 standard deviation of $J_S(t)/J_S(o)$ for hematite and maghemite, respectively). With the technique used here, only 0.1% ($<$1 micrometer thick oxidation layer on a millimeter thick layer of magnetite) conversion was required. To produce $>$3-15% oxidation would have required 30-150 times longer irradiation periods than required for the detection of 0.1% conversion, and under the conditions of the Morris and Lauer experiment irradiation times would again not have been long enough.

We think that these two factors explain the differences between the Morris and Lauer (6) results and the results reported here. The potential loss of H_2O by this process on Mars over geologic time would be a factor of 10^0-10^3 times greater than the amount predicted to have been lost by exospheric escape. It may be the principal reservoir for H_2O that has been released to the atmosphere over geologic time.

Acknowledgement. This research was supported by NASA Grants NSG7405 and NAGW570 to the University of Massachusetts.

References.

1 Huguenin, R.L. (1973) J. Geophys. Res., 78, p. 8481-8493.
2 Huguenin, R.L. (1973) J. Geophys. Res., 78, p. 8495-8506.
3 Huguenin, R.L. (1974) J. Geophys. Res., 79, p. 3895-3905.
4 Huguenin, R.L. (1976) Icarus, 28, p. 203-212.
5 Huguenin, R.L. (1982) J. Geophys. Res., 87, p.10,069-10,082.
6 Morris, R.V. and Lauer, H.V. Jr. (1980) Geophys. Res. Lett., 7, p. 605-608.
7 Huguenin, R.L., Prinn, R.G., and Maderazzo, M. (1977) Icarus, 32, p.270-298.
8 Poole, C. (1977) Thesis, MIT Dept. Physics.
9 Bagus, P.S., Brandle, C.P., Chuang, T.J., and Wandelt, K. (1977) Phys. Rev. Letters, 39, p. 1229-1232.